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MERCURY BROMIDE RECONSTITUTION IN THE
HgBr LASER SYSTEM

C. S. Liu

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Final Report Covering
May 15, 1983 to June 15, 1984

Contract No. N00014-83-C-0375
Office of Naval Research

September 11, 1984

Westinghouse R&D Center
1310 Beulah Road
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I. INTRODUCTION

This report summarizes research work performed at the Westinghouse R&D Center under Contract No. N0014-83-C-0375 for the period between May 15, 1983, and June 15, 1984. The major effort was to perform experimental life studies of an UV pre-ionized HgBr laser and reconstitute the reaction products such as Hg and Hg_2Br_2.

During past years, we had conducted extensive experimental lifetime studies of a small scale HgBr laser. From these experiments, we selected suitable materials[1] for laser construction, developed procedures to fabricate and fill the laser tube, and finally, we lifetested[2,3] the laser for over 5×10^6 shots. Those results indicate that pinhole-free gold plated nickel is chemically inert to the $HgBr_2$ discharge and can be used for constructing long-lived high prf HgBr lasers. However, for a large system it is difficult to plate the base metal with pinhole free gold. It is this motivation for developing a $HgBr_2$ recovery system.

In this report, we describe the construction of a long-lived, high prf HgBr laser with a built-in $HgBr_2$ reconstitution system and present experimental test data which confirm our theoretical predictions. Finally we recommend the future design of a practical 10^{10} shots HgBr laser.

1

II. CHEMICAL REACTIONS IN HgBr LASERS

The chemical reactions taking place in an HgBr laser is quite similar
to that of commercial metal halide lamps. During the laser discharge,
electron impact dissociates and excites the $HgBr_2$ and then the dissociated
species recombine with one another to reform $HgBr_2$. In principle, these
dissociation and re-association processes can go on forever, providing
the re-association rate is fast enough to recovery all the fragments
and there is no loss of mercury or bromine due to chemical reactions
with other metals such as electrode materials. The most important rule
one should keep in mind when selecting materials is that the metal
bromide of the metals used in the laser should be much less stable than
that of the $HgBr_2$ at the laser operating temperature. In this way, the
metal used will not rob the bromine or Hg from $HgBr_2$ molecules. The
bromine cycle will be kept within the $HgBr_2$ system itself. Thus, the
HgBr laser can have a long operating life. For this to be valid, the
device must be made under well controlled, clean conditions so that
impurities such as oxygen do not enter the cycle and change the course
of reactions.

The typical operating temperature of an HgBr laser is between 150 and
$200^{\circ}C$. It is important to use materials in the laser tube which are
chemically inert to $HgBr_2$, HgBr, Hg, Br and Br_2 at such temperatures.
In selecting materials, simple thermochemical calculations are useful
to eliminate the unsuitable materials, but these calculations are not
sufficiently adequate to predict the chemical stability of the materials
chosen because they do not include non-equilibrium conditions, nor take
into account the excited state chemistry, chemical transport reactions
and photochemical or ionic effects occurring in laser discharges. The
ultimate means in selecting the materials of the HgBr laser is experi-
mental chemical compatibility study. Nevertheless, thermodynamic

2

calculations can eliminate many candidates and thus reduce the
experimental effort to a manageable level.

Glasses, quartz and ceramic oxides are inert to $HgBr_2$, HgBr, Hg, Br
and Br_2 under thermodynamic equilibrium conditions, thus they can be
used as HgBr laser tube as insulator materials. Polyamides are also
inert to the $HgBr_2$ gas when they are shielded from UV radiation and
corona. For metals, the tendency of reactions with $HgBr_2$, HgBr, Hg,
Br and Br_2 can be predicted by calculating the free energy change for
each of the participating compounds. Table 1 lists the free energy
changes[4] for the chemical reactions of

$$\frac{X}{2} HgBr_2 + M \rightarrow M Br_x + \frac{X}{2} Hg$$
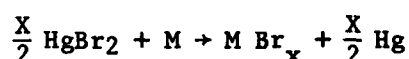
where M is the metal to be used in HgBr lasers. Al, Cr, Ni, Ta and
Ti have negative values of free energy change; therefore, they are
definitely not suitable for HgBr lasers. Since the free energy change
for Mo, W, Au, Pt or Re has a large positive value, the metal-$HgBr_2$
reaction is negligible. For instance, if one has chosen tungsten as a
base metal to build a HgBr laser operated at 500°K, the free energy
change, ΔF, for the reaction $5/2 \, HgBr_2 + W \rightarrow W Br_5 + 5/2 \, Hg$ is 56,000
calories. The equilibrium constant, K, can be calculated as follows:

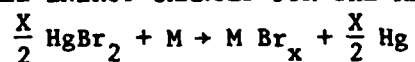$$K = \exp\left(-\frac{\Delta F}{RT}\right) = 3 \times 10^{-24}$$

The equilibrium constant, K, is defined as

$$K = \frac{\left(P_{WBr_5}\right) \cdot \left(P_{Hg}\right)^{5/2}}{\left(P_{HgBr_2}\right)^{5/2}}$$

Since $P_{HgBr_5} = 0.1$ atm (at 500°K)[5] we calculate

3

Table 1

THE FREE ENERGY CHANGES FOR THE REACTIONS

$$\frac{X}{2} HgBr_2 + M \rightarrow M Br_x + \frac{X}{2} Hg$$

M	M Br$_x$	ΔF 500°K (kcal)
Al	AlBr$_3$	-65
Au	AuBr$_3$ (AuBr, AuBr$_2$)	+53 (+17, +37.1)
C	CBr$_4$	+49.4
Cr	CrBr$_2$ (CrBr$_3$)	-29.5 (-26)
Mo	MoBr$_5$ (MoBr$_4$, MoBr$_3$, MoBr$_2$)	+54 (+40, +26, +13)
Ni	NiBr$_2$	-7.5
Pt	PtBr$_4$ (PtBr$_3$, PtBr$_2$, PtBr)	+54 (+41.5, 27, 13)
Re	ReBr$_3$	+38.3
Ta	TaBr$_5$	-37
Ti	TiBr$_4$ (TiBr$_3$, TiBr$_2$)	-64 (-66, -50)
W	WBr$_5$ (WBr$_6$, WBr$_4$, WBr$_2$)	+56 (+88, +50, +23)

4

$$[P_{WBr_5}] \cdot [P_{Hg}]^{5/2} = 9.5 \times 10^{-27}$$

Since $P_{WBr_5} \sim 0.01$ atm (at 500°K) the equilibrium pressure of Hg is

$$P_{Hg}\big|_{eq} \sim 2.5 \times 10^{-10} \text{ atm}$$

As the free-energy change for tungsten and $HgBr_2$ reaction is positive, 56,000 calories, the tungsten reduction of $HgBr_2$ will be negligible. The thermodynamic equilibrium calculations indicate that as soon as the partial vapor pressure of Hg or $HgBr_2$ reaches $\sim 2.5 \times 10^{-10}$ atm at 500°K, all the chemical reactions of $HgBr_2$ and tungsten will cease. However, in the case of using Ni as the material for a HgBr laser, the free-energy change, ΔF, of the chemical reaction of $Ni + HgBr_2 \rightarrow NiBr_2 + Hg$ is negative 7,500 calories. The equilibrium constant, K, is

$$K = 1.9 \times 10^3$$

The equilibrium pressure of Hg is calculated to be 1.9×10^2 atm in order to stop the chemical reaction. Since the vapor pressure of Hg at 500°K is only about 0.06 atm[6] (and cannot reach 2×10^2 atm), the chemical reaction of $HgBr_2$ and Ni will proceed indefinitely until all the $HgBr_2$ is totally reduced by the nickel. Therefore, nickel is not a suitable metal for use in HgBr lasers.

Near the electrode region, chemical reactions become more complicated. There will be present $HgBr_2$, HgBr, Hg and free bromine. Since HgBr is less stable than $HgBr_2$, any metal which is inert to $HgBr_2$ should also be inert to HgBr. One concern when using noble metals is that they have a tendency to amalgamate with Hg, which may cause severe problems. The amalgamation of Hg can quickly deplete the Hg from $HgBr_2$ as well as reduce the mechanical strength of the material used. Because the Hg-Br chemical bond is stronger than that of Hg-X (where X - Au, Pt, Re), the free bromine breaks down the Hg-X alloy bond to form $HgBr_2$ and prevents

5

the formation of the Hg-X. However, if one loses bromine from the HgBr$_2$ in the laser tube by other reactions then excess mercury will be tied up with Au or Pt. Unfortunately, free bromine reacts with almost any metal in contact with it at 500°K. From the equilibrium constants of the reactions

$$MBr_x(C) \rightarrow M(C) + \frac{X}{2} Br_2 \text{ (g)}$$
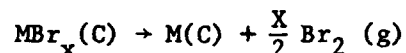
one can predict the direction in which the reaction proceed under certain conditions. The equilibrium constants and the equilibrium pressures of Br$_2$ for the above reactions are listed in Table 2.[4] The thermodynamic calculations for NiBr$_2$ indicates that even if the partial vapor pressure of Br$_2$ is as low as 7.2×10^{-17} atm, the reaction still proceeds toward left, in the above equation, namely:

$$Ni(C) + Br_2(g) \rightarrow NiBr_2(C)$$
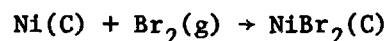
In the case of gold, until the partial vapor pressure of Br$_2$ reaches 3.83 atm (at 500°K), the reaction will proceed quickly toward right. That is, the AuBr$_3$ will continuously dissociate into Au and Br$_2$ until the bromine reaches its equilibrium pressure of 3.83 atm. In the HgBr laser, the free bromine pressure will only reach 10^{-4} to 10^{-5} atm. Therefore as far as bromine reaction is concerned, gold is excellent, platinum and rhenium are good, molybdenum and tungsten are questionable and nickel is not suitable for the HgBr laser system.

There are metals in which the reaction produces a protective film on the surface to retard further reaction (passivation). Thus, materials such as Ni, Al and stainless steel can sometimes be used even though the thermodynamics are unfavorable. However, such metals can only be used as the container material, not as the electrode since the discharge will readily destroy the protective coating.

Table 2

EQUILIBRIUM CONSTANTS, Kp, FOR THE REACTIONS

$$MBr_x(c) \rightarrow M(c) + \frac{X}{2} Br_2(g)$$
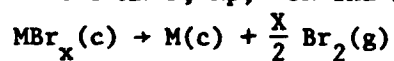
$\underline{MBr}_x$	$\underline{K}_p\underline{(500°K)}$	$\underline{P}_{Br_2}\big|$ equilibrium
$AuBr_3$	$P_{Br_2}^{1.5} = 7.5$	3.83 atm
CBr_4	$P_{Br_2}^{2} = 10^{6.7}$	2321 atm
$MoBr_5$	$P_{Br_2}^{2.5} = 2.8 \times 10^{-14}$	3.8×10^{-6} atm
$NiBr_2$	$P_{Ni} = 7.2 \times 10^{-19}$	7.2×10^{-19} atm
$PtBr_4$	$P_{Pt}^{2} = 7.6 \times 10^{-7}$	8.7×10^{-4} atm
$ReBr_3$	$P_{Re}^{15} = 2.8 \times 10^{-6}$	2×10^{-4} atm
WBr_5	$P_{Br_2}^{2.5} = 2.1 \times 10^{-13}$	8.5×10^{-6} atm

After a careful analysis one can conclude that the metal used for electrodes should be either gold or platinum, metals used near the laser discharge could be gold or platinum plated nickel and metals situated far away from the electrodes could be even relaxed to Mo, W or stainless steel. However, one must always keep in mind that no matter what materials he is going to use, a vacuum tight ultra-clean system is the key to the long-lived HgBr laser. The required cleanliness and chemical inertness is difficult to achieve in practice.

III. HgBr$_2$ RECONSTITUTION SYSTEM

In a HgBr laser, the discharge pulse dissociatively excites the HgBr$_2$
generating various free redicals such as HgBr(B), HgBr(X), Br Br$_2$, Hg*,
Hg, etc. Between the discharge pulses, they will recombine with one
another to reform the HgBr$_2$. The rate of the association is a function
of temperature, temperature distribution, vapor density, buffer gas
pressure, current density, gas flow rate and geometry. For a continuously
pulsed laser, a steady state condition will be established and each
species will maintain a certain equilibrium pressure. If the metals
used in the laser tube are not totally inert, there will be a continuous
buildup of Hg and HgBr vapors, causing a gradual deterioration of laser
performance. The ultimate remedy is to provide a bromine source which
can react with the Hg and HgBr vapor to reconstitute the HgBr$_2$. It is
obvious that one cannot use free bromine because of its uncontrollable
high vapor pressure at the laser operating temperature which not only
affects the discharge but also absorbs laser photons. However, some
metal bromides having very low vapor pressure at the laser operating
temperature can be used as a bromine source. If the metal bromide
used is less stable in comparison to the HgBr$_2$ then the free Hg will
grab the bromine from the metal bromide to form HgBr$_2$ and leave the
metal precipitate in the recovery chamber. Therefore two major criteria
in selecting the metal bromide for the reconstitution process are (1)
very low vapor pressure at the laser operating temperature and (2)
chemically less stable in comparison with the HgBr$_2$. Figure 1 shows a
schematic diagram of the HgBr$_2$ reconstitution system for the HgBr laser.
A high speed blower in the laser chamber provides gas circulation fast
enough for high pulse repetition rate operation. From a separate, low
throughput, flow loop, the gas is pumped out through a reconstitution
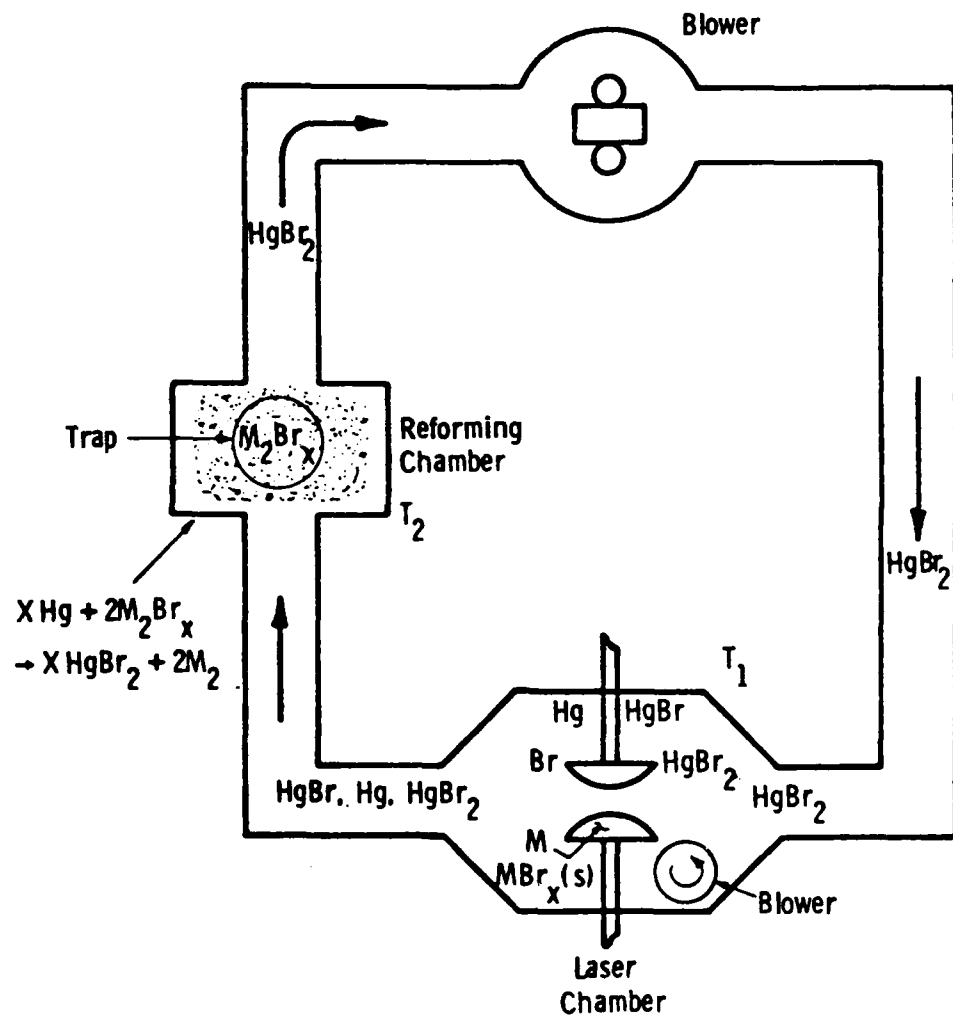chamber which contains the desired metal bromide. The operating conditions
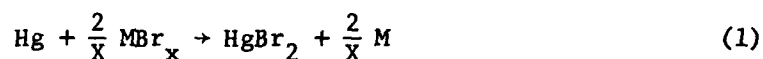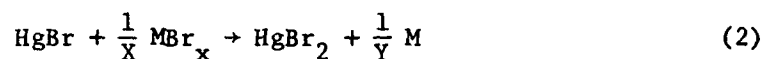
9

Figure 1 Mercuric Halide Recovery System
(Not to scale)

of the reconstitution system, such as temperature and flow rate, are optimized according to the rates of the following chemical reactions:

$$Hg + \frac{2}{X} MBr_x \rightarrow HgBr_2 + \frac{2}{X} M \tag{1}$$

and

$$HgBr + \frac{1}{X} MBr_x \rightarrow HgBr_2 + \frac{1}{Y} M \tag{2}$$

Since the reconstitution process takes place under local thermodynamic equilibrium conditions, the thermochemical calculations are valid in this region. Table 3[4] lists the possible candidates for the $HgBr_2$ reconstitution according to their thermodynamic data. Column A indicates the type of bromides used, and column B and C indicate the free energy changes for reaction 1 and reaction 2, respectively. The free energy values in columns B and C are the measures of the tendency

Table 3

Possible Candidates for the $HgBr_2$ Reconstitution Process

Bromide	ΔF for $Hg + \frac{2}{X} MBr_x = HgBr_2 + \frac{2}{X} M$ (in cal)	ΔF for $HgBr + \frac{1}{X} MBr_x = HgBr_2 + \frac{1}{X} M$ (in cal)
$ReBr_3$	−26,000	−13,400
$MoBr_2$	−13,000	− 7,000
$MoBr_3$	−17,400	− 9,100
$MoBr_4$	−20,000	−10,400
$MoBr_5$	−21,600	−11,200
WBr_2	−23,000	−11,900
WBr_4	−25,000	−12,900
WBr_5	−22,400	−11,600
$PtBr_2$	−27,000	−13,500

for the reactions to proceed under the stipulated conditions. Large negative value of ΔF means that the reconstitution process will proceed rapidly. Among these bromides, only $MoBr_2$ and WBr_5 are readily available. Therefore, our reconstitution tests were limited to these two bromides. Figure 2 shows the free energy changes of reactions as a function of temperature calculated from the thermodynamic data. The reconstitution rates increase with increasing temperature. However, the operating temperature is limited by the vapor pressure and the chemical stability of the bromide used. The upper limit of the operating temperature of a reconstitution system using WBr_5 or $MoBr_2$ is set by its vapor pressure (no more than 10^{-4} atm) and it is 410°K for WBr_5 or 600°K for $MoBr_2$ respectively. A simple $HgBr_2$ reconstitution test setup is shown in Figure 3. In the first experiment, we conducted a test without any reconstitution agent in the tube. One end of a U-shaped tube with $HgBr_2$ and clean Ni foil in it was heated to 200°C. As soon as the $HgBr_2$ started to vaporize, the bright metallic Ni foil turned to a yellow dull color due to the formation of $NiBr_2$ on the surface. At the cooler end of the U-shaped tube we collected $HgBr_2$, Hg_2Br_2 and Hg but no $NiBr_2$ or Ni. Then we performed similar tests with $MoBr_2$ or WBr_5 powder in the tube for the purpose of reconstitution. At 200°C, both $MoBr_2$ and WBr_5 worked very effectively. Neither Hg nor Hg_2Br_2 were detected in the cold zone. Since WBr_5 had $\sim$ 1 torr vapor pressure at 200°C, small amounts of WBr_5 powder were condensed near the cold spot. In a practical system, the $MoBr_2$ is much preferred to the WBr_5 because of its low vaporization.
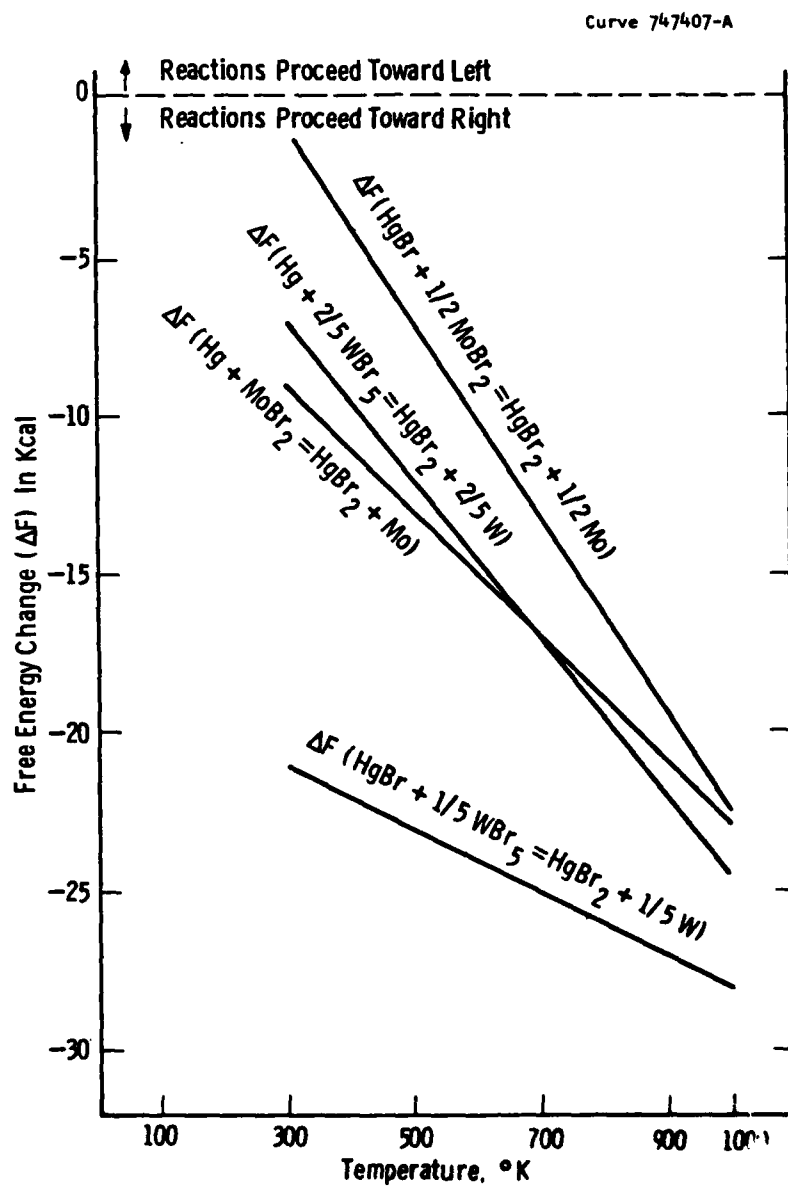
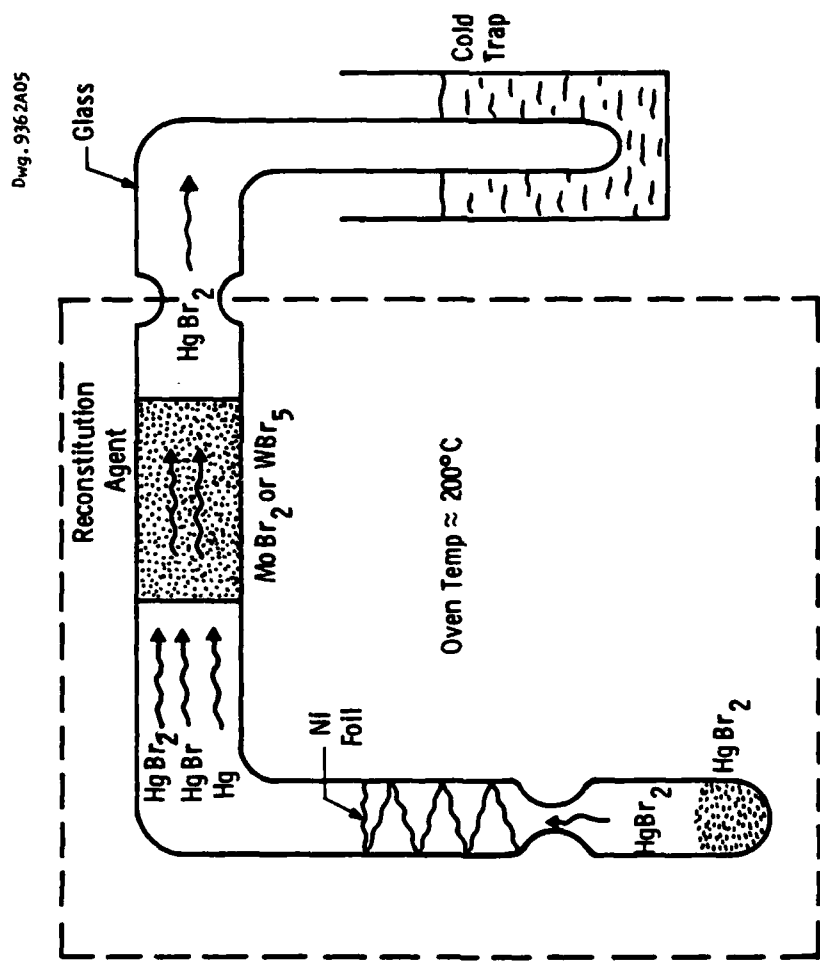Figure 2   Free Energy Change, ΔF, as a Function of Temperature

Figure 3 Simple HgBr$_2$ Reconstitution Test

14

IV. HgBr LASER LIFE TEST

The high PrF sealed-off HgBr laser with a $HgBr_2$ reconstitution system is shown in Figure 4. The laser tube was fabricated from a six-inch glass pipe with two #304 stainless steel end plates. The electrode supporting structures and gas circulating blower were made of gold-plated nickel. The front surfaces of the electrodes were capped with 5 mil gold foil. The UV preionization was generated from an array of sparks formed by platinum wires. The discharge gases which consist of $\sim$ 10 Torr of $HgBr_2$ vapor, 100 Torr of N_2 and 900 Torr of neon flowed through two parallel electrodes with the aid of a squirrel cage blower.

From previous $HgBr_2$ discharge tests[2], we observed high loss rates of gold and platinum from the main electrodes and UV preionizers which made us aware of potential problems resulting from metallic coating of optics. In this laser tube, we inserted two glass baffles to confine the gas circulation which significantly reduced the possibility of the coating the optical windows.

The laser gas is pumped out from one of the end plates through a $HgBr_2$ reconstitution chamber which contains $MoBr_2$ powder. The operating temperature and flow rate of the reconstitution chamber are pre-optimized according to the thermodynamic equilibrium calculations. The entire experiment was conducted at a pulse repetition rate of 50 Hz. The input energy was stored in four 2,700 pf ceramic capacitors charged to 10 kV through a L-C inversion circuitry. The energy was discharged through grounded grid EG&G 3202 thyratrons. During the test, a vacuum photo-diode was used to monitor the laser output. The laser discharge fluorescence without lasing was also periodically measured.
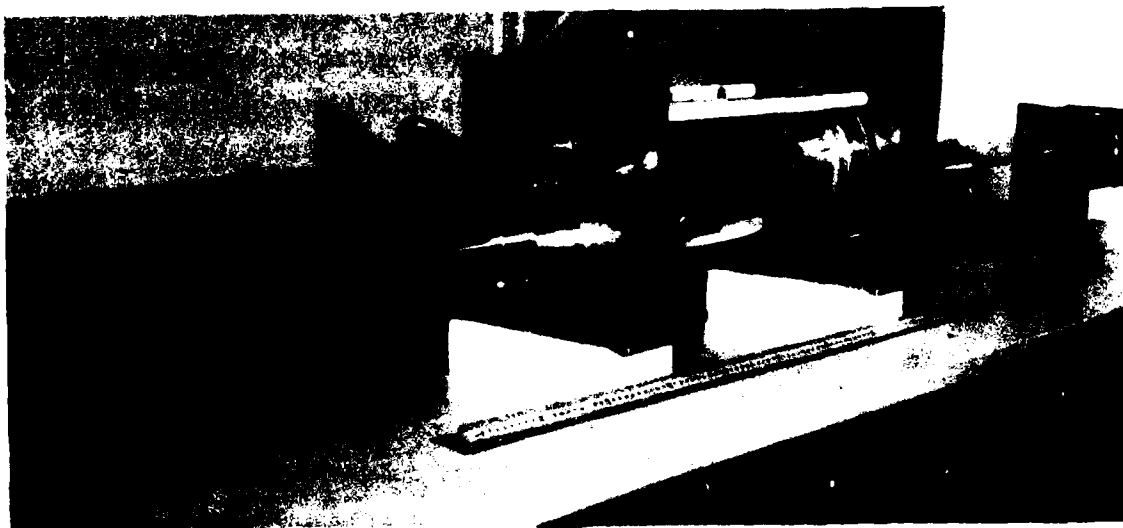
15

Figure 4   High PRF HgBr Laser with a $HgBr_2$ Reconstitution System

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Since the active length of this laser was only 12 cm, the laser was always operated near its threshold which provided the most sensitive way for monitoring the degradation of the laser output. The output stability from pulse to pulse varied less than 15% while the long term stability changed less than 5% until $\sim 3 \times 10^7$ pulses. The life-test was temporarily interrupted twice because of thyratron failures. During the repair of the last thyratron failure, we modified the reconstitution system by slightly increasing the flow. Figure 5 shows the laser output as a function operating life. No sign of laser deterioration has been observed and the laser output remained constant at 392 μJ per pulse. A slight blackening on the preionizer rods indicated a material loss due to sputtering. Material loss from gold electrodes caused by sputtering was undetectable. The stainless steel end plates were placed purposely to generate some reaction products, so that one can test the effectiveness of the reconstitution system. After 3×10^7 pulses, we noticed some discoloration of the stainless steel plates but no sign of any effect on the HgBr laser performance. Aside from the thyratron, capacitors and some unexpected minor mechanical difficulties, the HgBr laser tube had no indications of any deterioration caused by chemical reactions. We firmly believe that a long-lived HgBr laser can be realized by using right material for the laser tube and installing a $HgBr_2$ reconstitution system to recover the bromine loss.
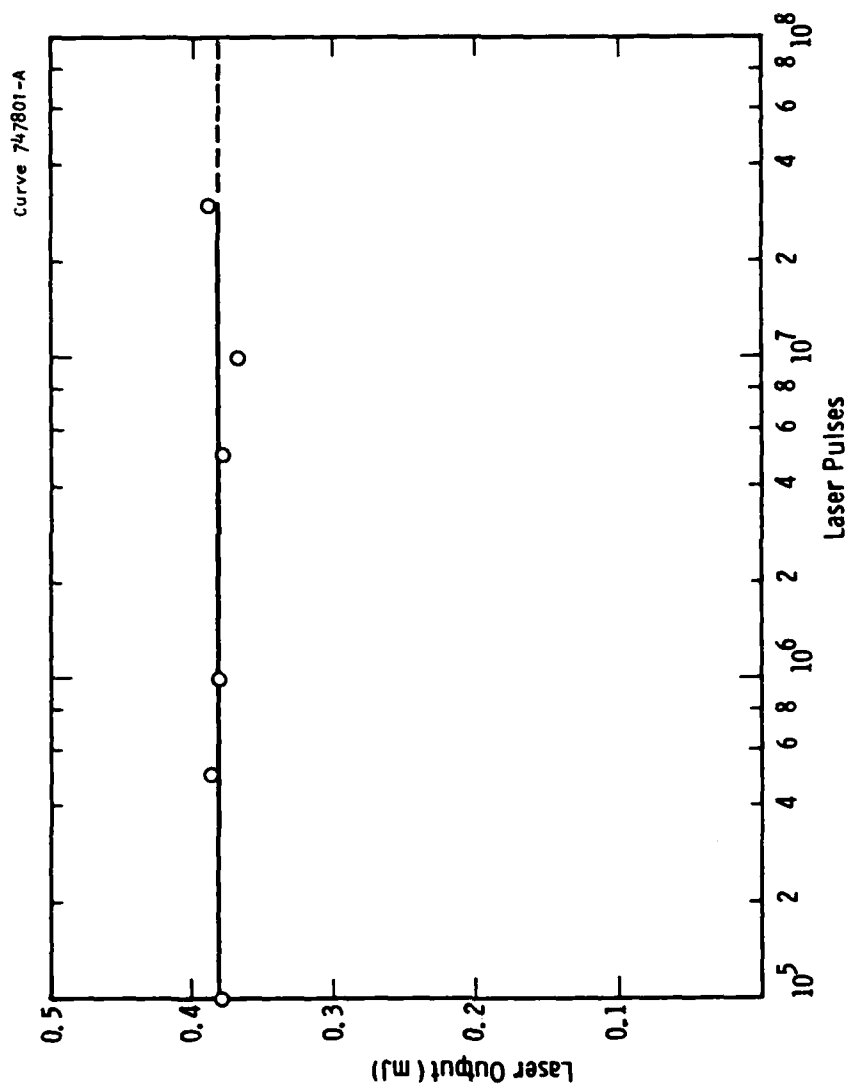
17

Figure 5 HgBr Laser Output vs. Operating Life

SUMMARY & RECOMMENDATIONS

The previous laser discharge study and laser lifetest indicated that
a pinhole-free gold plated nickel was chemically inert to HgBr laser
gases. Without any reconstitution system installed in a gold plated
HgBr laser, the laser itself can last over 5×10^6 shots.[3] For a
larger laser system, pinhole-free gold plating becomes very difficult
if not impossible; therefore, a reconstitution system for $HgBr_2$ was
installed to take care of the pinhole problem. To exaggerate the
pinhole in the gold plating, we purposely used an uncoated end-plate
in a gold plated HgBr laser for lifetest and it has operated over
3×10^7 shots without any sign of laser deterioration. This test
made us firmly believe that a gold-plated HgBr laser with a $HgBr_2$
recovery system can certainly last 10^8 shots and beyond. We did not
test the system to failure in the present program; this would have to
be done to determine the ultimate life of the HgBr laser system."·
However, we are encouraged and optimistic about the lifetest result
of our HgBr laser, and we believe that 10^{10} shots for HgBr lasers is
obtainable. In addition, the same technique can be easily extended
the the XeCl laser system. If one can install a HCl reconstitution
system for XeCl laser instead of replacing HCl every so often,[7] the
whole laser system will be lighter, simpler and last longer than the
present system.

This report was typed by Toni McElhaney.

19

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